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(54) BLENDED POLYMER ELECTROLYTE, ELECTROLYTIC MEMBRANE HAVING THE ELECTROLYTE AS MAIN COMPONENT, AND MEMBRANE /ELECTRODE JUNCTION CONTAINING THE ELECTROLYTE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyelectrolyte superior in ionic conductivity and durability and suitable for a proton exchange membrane or the like of a fuel cell, and provide an electrolytic membrane having the electrolyte as the main component, and a membrane/electrode junction containing the electrolyte.

SOLUTION: This is a blended polymer electrolyte composed of a mixture of (a) polybenzoxazole or polybenzthiazole having not less than one kind of groups selected from a sulfonic acid group and its salts or a phosphonic acid group and its salts, and (b) a basic polymer having at least one kind of groups selected from groups composed of a sulfonic acid group and its salts, a phosphonic acid group and its salts, and a carboxylic acid group and its salts.

LEGAL STATUS

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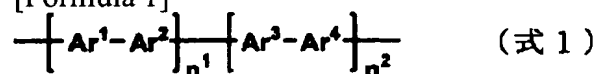
CLAIMS

[Claim(s)]

[Claim 1] (a) a sulfonic group -- and -- the -- a salt -- or -- phosphonic acid -- a radical -- and -- ** -- a salt -- from -- becoming -- a group -- choosing -- having -- a kind -- more than -- a radical -- a molecule -- inside -- one -- a piece -- more than -- having -- poly -- benzoxazole -- or -- poly -- bends -- a thiazole -- (-- b --) -- a sulfonic group -- and -- the -- a salt -- phosphonic acid -- a radical -- and -- the -- a salt -- a carboxylic acid -- a radical -- and the -- a salt -- from -- becoming -- a group -- choosing -- having -- a kind -- more than -- a radical -- a molecule -- inside -- one -- a piece -- more than -- having -- basicity -- a polymer -- mixture -- from -- becoming -- things -- the description -- ** -- carrying out -- blend polymer -- an electrolyte .

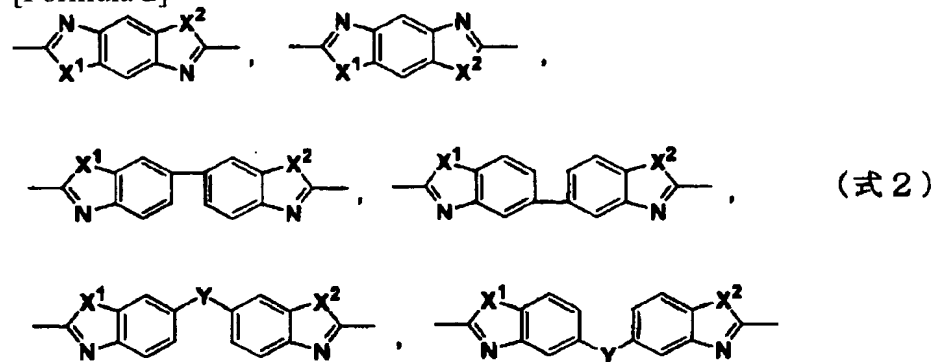
[Claim 2] Poly benzoxazole or the poly bends thiazole is the following general formula (1) or (5).;

[Formula 1]



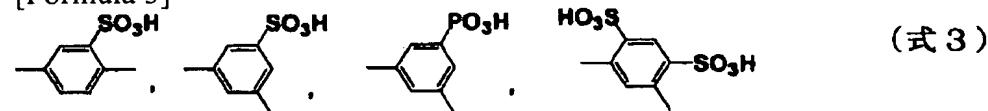
[type (1) means that the repeat unit which consists of Ar1 and Ar2, and the repeat unit which consists of Ar3 and Ar4 have connected with random or a block. The inside of a formula, and Ar1 and Ar3 are the following general formula (2).;

[Formula 2]



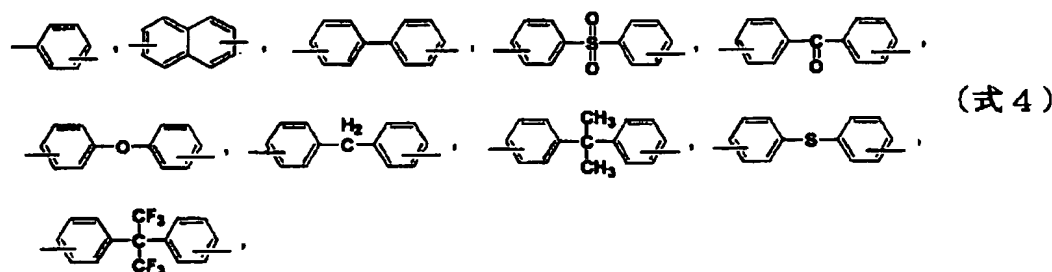
The residue more than a kind which comes out and is chosen from the residue expressed is expressed, and even if Ar1 and Ar3 are the same, they may differ. X1 and X2 express O or S. Y expresses CH₂, C (CH₃)₂, C (CF₃), or S (=O)₂ [O, S, C=O and]. Ar2 is the following general formula (3).;

[Formula 3]



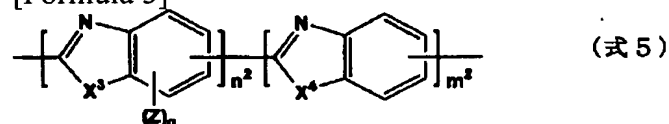
The residue more than a kind which comes out and is chosen from the group expressed is expressed. Ar4 is the following general formula (4).;

[Formula 4]



The residue more than a kind chosen from the group which comes out and consists of residue expressed is expressed. n1 expresses the integer of 1-10000, and m1 expresses the integer of 0-10000, respectively.]

[Formula 5]



[type (5) means that each repeat unit has connected with random or a block. X3 and X4 express either S atom or O atom among a formula, and even if these are the same, they may differ. Z expresses SO3H set, PO3H2 set, and one or more sorts of radicals chosen from those salts. n2 expresses the integer of 1-10000, and, as for m2, q expresses the integer of 0-10000 for the integer of 1-3, respectively.] The blend polymer electrolyte according to claim 1 which comes out and is characterized by what is expressed.

[Claim 3] The blend polymer electrolyte according to claim 1 or 2 characterized by being one or more sorts of compounds chosen from the group which a basic polymer becomes from the polymer of 2-vinylpyridine and its copolymer, 4-vinylpyridine, the copolymer, polybenzimidazole and the poly quinoline, and the poly quinoxaline.

[Claim 4] The electrolyte membrane which uses a blend polymer electrolyte according to claim 1 to 3 as a principal component.

[Claim 5] The film / electrode zygote characterized by including a blend polymer electrolyte membrane according to claim 1 to 3 in the film and/or an electrode layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a polymer electrolyte useful as polyelectrolyte film, the electrolyte membrane which makes it a principal component, and the film / electrode zygote using this electrolyte.

[0002]

[Description of the Prior Art] A water electrolyzer and a fuel cell can be mentioned as an example of the electrochemical equipment which uses a solid polymer electrolyte as an ion conductor instead of a liquid electrolyte. The poly membrane used for these must be chemical, thermal, electrochemical, and dynamic sufficiently stable in proton conductivity as cation exchange membrane. For this reason, as what can be used over a long period of time, the perfluorocarbon-sulfonic-acid film which mainly makes "Nafion (trademark)" by U.S. Du Pont the example of representation has been used. However, if it is going to operate on the conditions exceeding 100 degrees C, membranous water content will fall rapidly, and also it becomes remarkable [membranous softening]. For this reason, in the fuel cell which uses as a fuel the methanol with which the future is expected, the degradation by the methanol transparency in the film happens, and sufficient engine performance cannot be demonstrated. Moreover, also in the fuel cell operated near 80 degree C by using as a fuel the hydrogen currently examined by the current Lord, it is pointed out as a failure of establishment of a fuel cell technique that membranous cost is too high.

[0003] As an electrolyte membrane which replaces the perfluorocarbon-sulfonic-acid film, the so-called hydrocarbon system polymer electrolyte which introduced acidic groups, such as a sulfonic group, into polymers, such as a polyether ether ketone, and polyether sulphone, polysulfone, is examined briskly in recent years. However, compared with perfluorocarbon sulfonic acid, it was easy to do hydration and swelling of a hydrocarbon system polymer electrolyte, and the problem was in the endurance under high humidity.

[0004] Mixing with a basic polymer is performed as one of the policies which control swelling. This tends to control swelling by constructing a bridge by the basic polymer in acidic groups, such as a sulfonic group in a polymer electrolyte. For example, the mixture (international public presentation patent official report WO 99/No. 54389 official report) of the polyether ether ketone (acid polymer) which has the polyether sulphone which has a sulfonic group, and a sulfonic group, and polybenzimidazole (basic polymer) etc. is known. However, neither sulfonation polyether sulphone nor a sulfonation polyether ether ketone had [that the desorption of the sulfonic group by the acid or heat tends to happen] enough endurance.

[0005] On the other hand, with the international public presentation patent official report WO 01/No. 01510 official report, it is 2 and 5-difluoro - A 3 and 6-disulfo terephthalic acid, 2, 2'-disulfo - Although 4 and the film which consists of mixture of the poly bends azole and polybenzimidazole using 4'-diphenyl ether dicarboxylic acid are indicated, the ion conductivity is not described.

[0006] Although the molecular complex of the polybenzimidazole to which the molecular complex of the polybenzimidazole which has a sulfonic group, and a thermosetting basic compound has a sulfonic group in the United States patent official report No. 6025439, and a basic thermoplastic polymer was indicated by the United States patent official report No. 5998550, respectively, electrochemical applications, such as an electrolyte, were not described in any. Moreover, the polybenzimidazole which has a sulfonic group had the fault that ion conductivity was lower than other polymer electrolytes, such as perfluorocarbon sulfonic acid, and polysulfone which has a sulfonic group, polyether sulphone, a polyether ether ketone.

[0007] Although endurance generally improved by mixing a basic polymer to an acid polymer, it was a thing at the sacrifice of the ion conductivity which the acid polymer originally had in coincidence.

[0008]

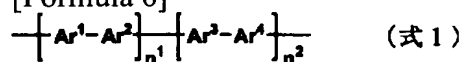
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the electrolyte membrane which uses the polyelectrolyte excellent in the suitable ion conductivity and the endurance for the proton exchange film of a fuel cell etc., and this electrolyte as a principal component, and the film containing this electrolyte / electrode zygote.

[0009]

[Means for Solving the Problem] this invention persons resulted in completion of a header and this invention that the polymer electrolyte in which the engine performance excellent in endurance, ion conductivity, etc. is shown, an electrolyte membrane and the film / electrode zygote was obtained by mixing the poly benzoxazole or the poly bends thiazole which has an acidic group, and the basic polymer which has an acidic group, as a result of repeating research wholeheartedly, in order to attain the above-mentioned purpose.

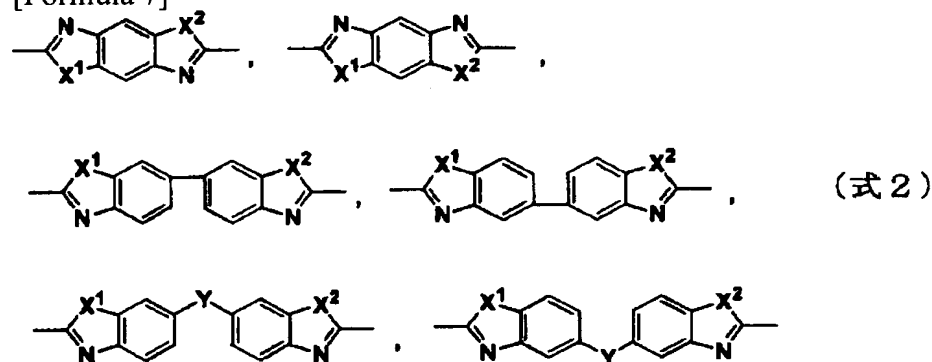
[0010] Namely, this invention (1), Blend polymer electrolyte which consists of mixture with the basic polymer which has a radical more than a kind chosen from the group which consists of the poly benzoxazole or the poly bends thiazole which has a radical more than a kind chosen from the group which consists of the (a) sulfonic group and its salt or a phosphonic acid radical, and a salt of ** in [one or more a molecule, the (b) sulfonic group and its salt, phosphonic acid radical and its salt, a carboxylic-acid radical, and its salt in / one or more / a molecule. (2) Poly benzoxazole or the poly bends thiazole is the following general formula (1) or (5).;

[Formula 6]



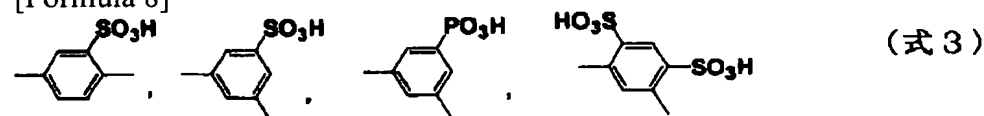
[type (1) means that the repeat unit which consists of Ar1 and Ar2, and the repeat unit which consists of Ar3 and Ar4 have connected with random or a block. The inside of a formula, and Ar1 and Ar3 are the following general formula (2).;

[Formula 7]



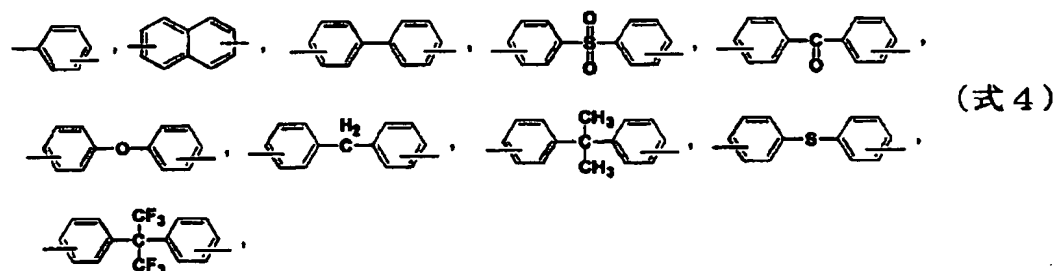
The residue more than a kind which comes out and is chosen from the residue expressed is expressed, and even if Ar1 and Ar3 are the same, they may differ. X1 and X2 express O or S. Y expresses CH₂, C (CH₃)₂, C (CF₃), or S (=O)₂ [O, S, C=O and]. Ar2 is the following general formula (3).;

[Formula 8]

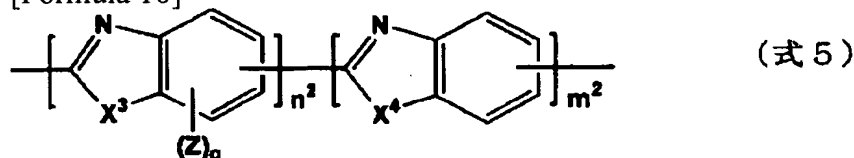


The residue more than a kind which comes out and is chosen from the group expressed is expressed. Ar4 is the following general formula (4).;

[Formula 9]



The residue more than a kind chosen from the group which comes out and consists of residue expressed is expressed. n_1 expresses the integer of 1-10000, and m_1 expresses the integer of 0-10000, respectively.]
[Formula 10]

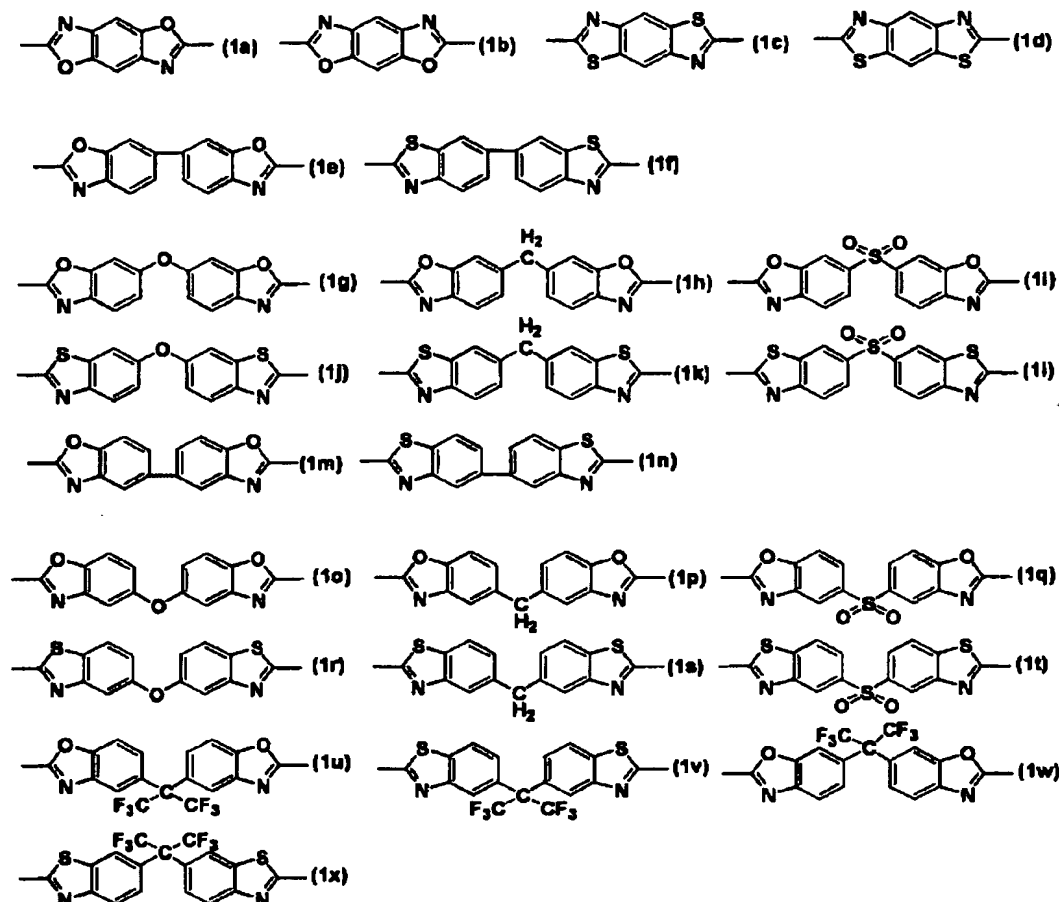


[type (5) means that each repeat unit has connected with random or a block. X_3 and X_4 express either S atom or O atom among a formula, and even if these are the same, they may differ. Z expresses SO_3H set, PO_3H_2 set, and one or more sorts of radicals chosen from those salts. n_2 expresses the integer of 1-10000, and, as for m_2 , q expresses the integer of 0-10000 for the integer of 1-3, respectively.] It is a blend polymer electrolyte given in (1) which comes out and is characterized by what is expressed. In a list (3) A basic polymer The polymer and its copolymer of 2-vinylpyridine, 4-vinylpyridine, and the copolymer, polybenzimidazole, the poly quinoline, It is characterized by being one or more sorts of compounds chosen from the group which consists of poly quinoxaline. (1) It is a blend polymer electrolyte given in (2). Or in a list (4) the electrolyte membrane which uses the blend polymer electrolyte of a publication as a principal component at either of (1) -3 -- it is -- a list -- (5) the film / electrode zygote characterized by including a blend polymer electrolyte membrane given in either of (1) - (3) in the film and/or an electrode layer -- it comes out.

[0011]

[Embodiment of the Invention] This invention is explained to a detail below. As a desirable example of Ar1 and Ar3 in a general formula (1), it is following (1a) - (1x).;

[Formula 11]

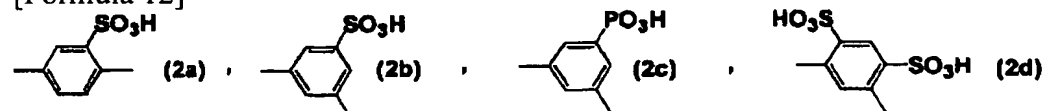


***** is not limited to this. (1b), (1c), (1e), (1f), (1g), and (1i) are more desirable, and (1b) and (1c) are the most desirable.

[0012] As an acidic group of Ar2, a sulfonic group, a phosphonic acid radical, carboxylic-acid radicals, and those salts can be mentioned. A sulfonic group and a phosphonic acid radical are desirable especially, and it is desirable in order that a sulfonic group may raise ion conductivity. As a compound which constitutes a salt, metal ions, such as sodium, a potassium, magnesium, calcium, barium, aluminum, iron, titanium, and copper, a low-molecular amine, an imidazole compound, a pyridine derivative, a quinoline derivative, etc. are mentioned. It is desirable that it is between 0-99-mol %, as for the salt in [all] an acidic group, it is more desirable that it is less than [20 mol %], and it is still more desirable that it is less than [10 mol %]. Although the two or more numbers of an acidic group should just be one or more pieces, there may be. A different acidic group like a sulfonic group and phosphonic acid may be intermingled.

[0013] An aromatic series radical expresses the radical containing one or more aromatic series rings. Although hetero atoms, such as the derivative, and O, S, may be included in the aromatic series radical, it is desirable to exist in that case as the substituent of an aromatic series ring and a radical which connects an aromatic series ring. [the alkyl group of carbon numbers 1-6 and] With an aromatic series ring, aromatic series heterocycles, such as a pyridine ring and a quinoline ring, are also included besides hydrocarbon groups, such as the benzene ring and a naphthalene ring. If the halogen has joined together by covalent bond in Ar2, in order to have a bad influence on an environment at the time of abandonment, as for Ar2, it is desirable that the halogen combined by covalent bond is not included. As for an acidic group, it is desirable to have combined with the aromatic series ring through other organic radicals, such as direct or an alkyl group. In order to control the desorption of an acidic group, it is desirable that electron releasing groups, such as an alkyl group, a ether group, and an amino group, have not combined with the aromatic series ring which the acidic group has combined. Although not limited especially, the radical expressed with following structure (2a) - (2d) as a desirable example of Ar2 can be mentioned.

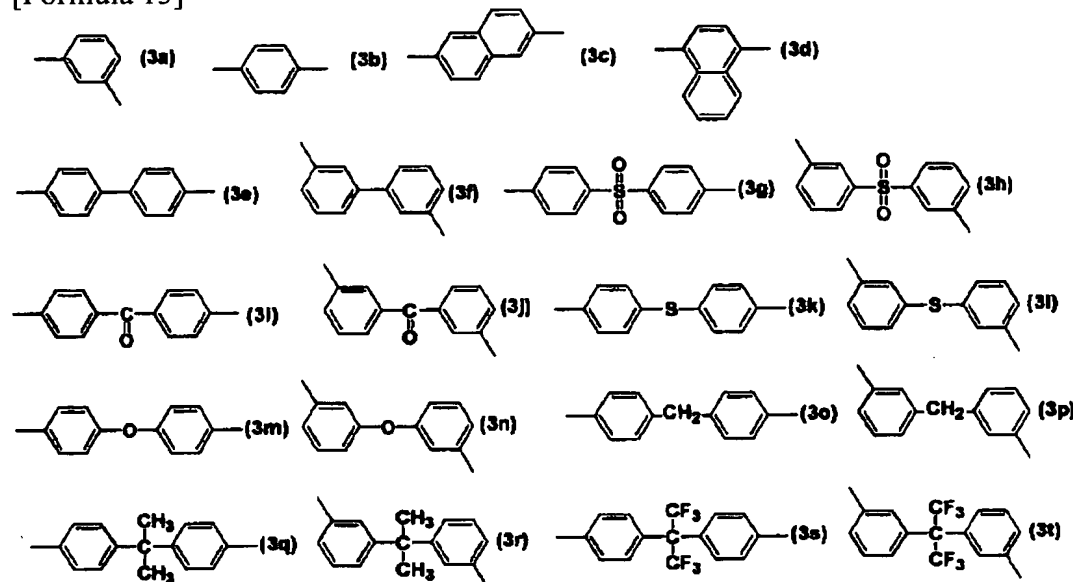
[Formula 12]



(2a) is more desirable especially.

[0014] As a desirable example of Ar₄, it is following residue (3a) - (3t).;

[Formula 13]

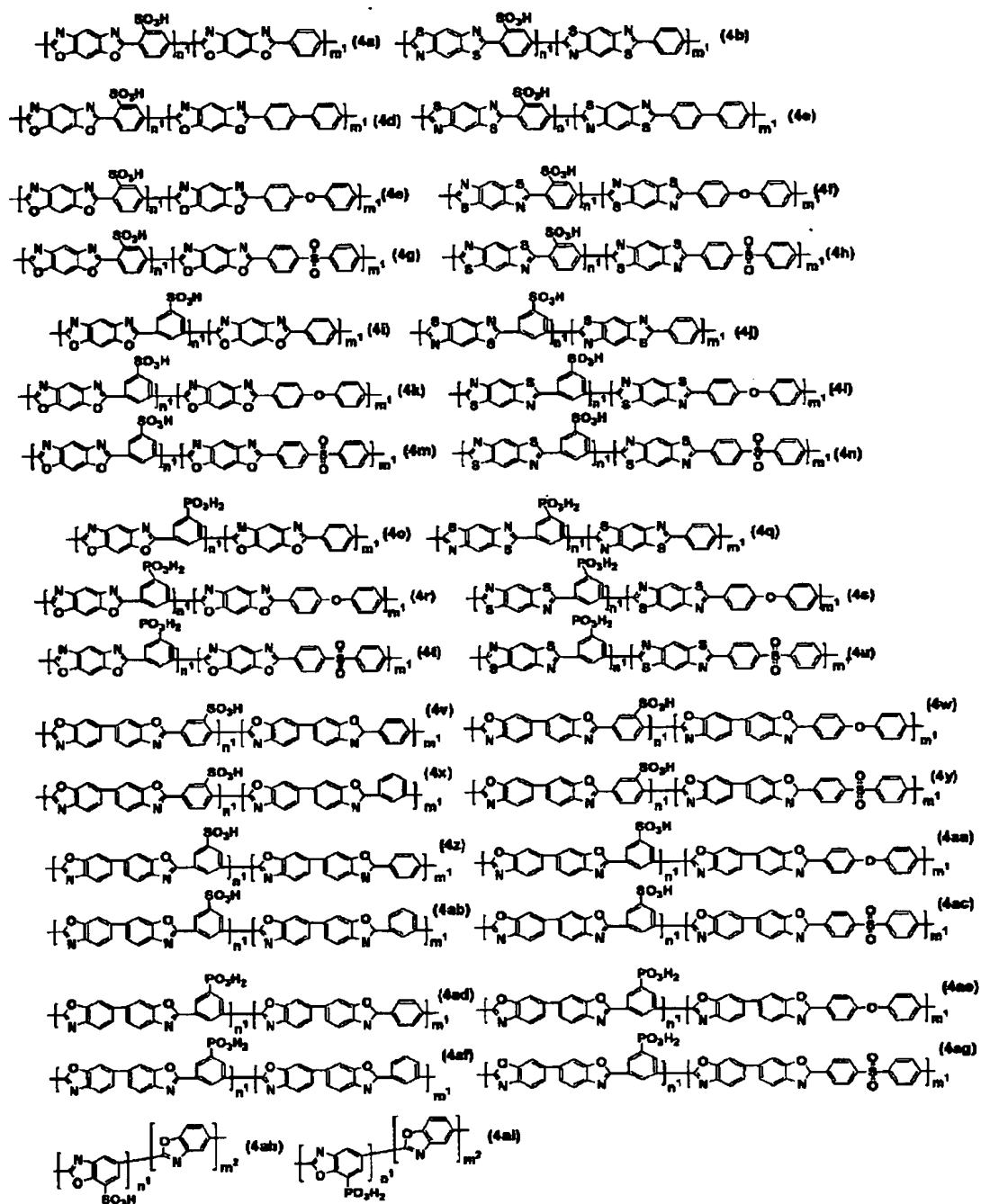


***** -- although things are made, it is not limited to these. Especially, (3b), (3e), (3g), (3k), and (3m) are more desirable, and (3b) and (3m) are the most desirable.

[0015] As for X₃ and X₄, it is more desirable that it is O, and it is the most desirable in order that that all are O may raise ion conductivity. As for Z, it is desirable that they are a sulfonic group or its salt. It is desirable in order to show the dynamics property that a molding object is desirable that n₁ and n₂ are ten or more, and it is still more desirable that it is 100 or more. Moreover, although m₁ and m₂ may be any value, since ion conductivity becomes it high that m₁/n₁ or m₂/n₂ are between 0-0.5, they are desirable, and still more desirable in it being between 0-0.2.

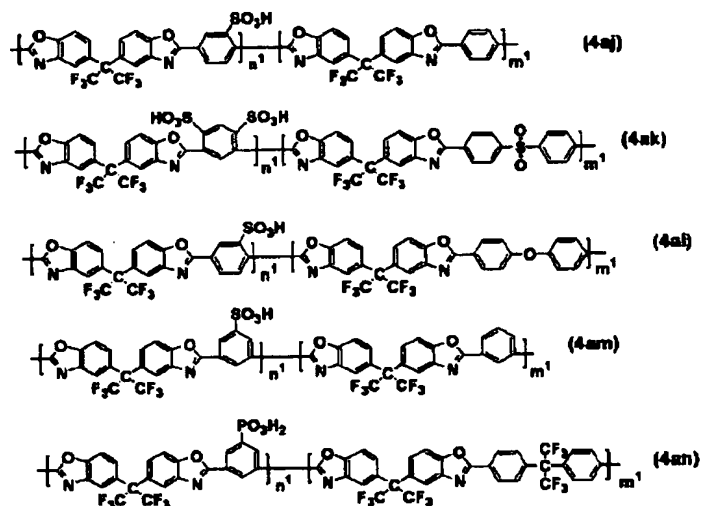
[0016] Although the desirable example of the acid polymer in this invention is shown in - (4a) below (4a), it is not limited to these.

[Formula 14]



[0017]

[Formula 15]



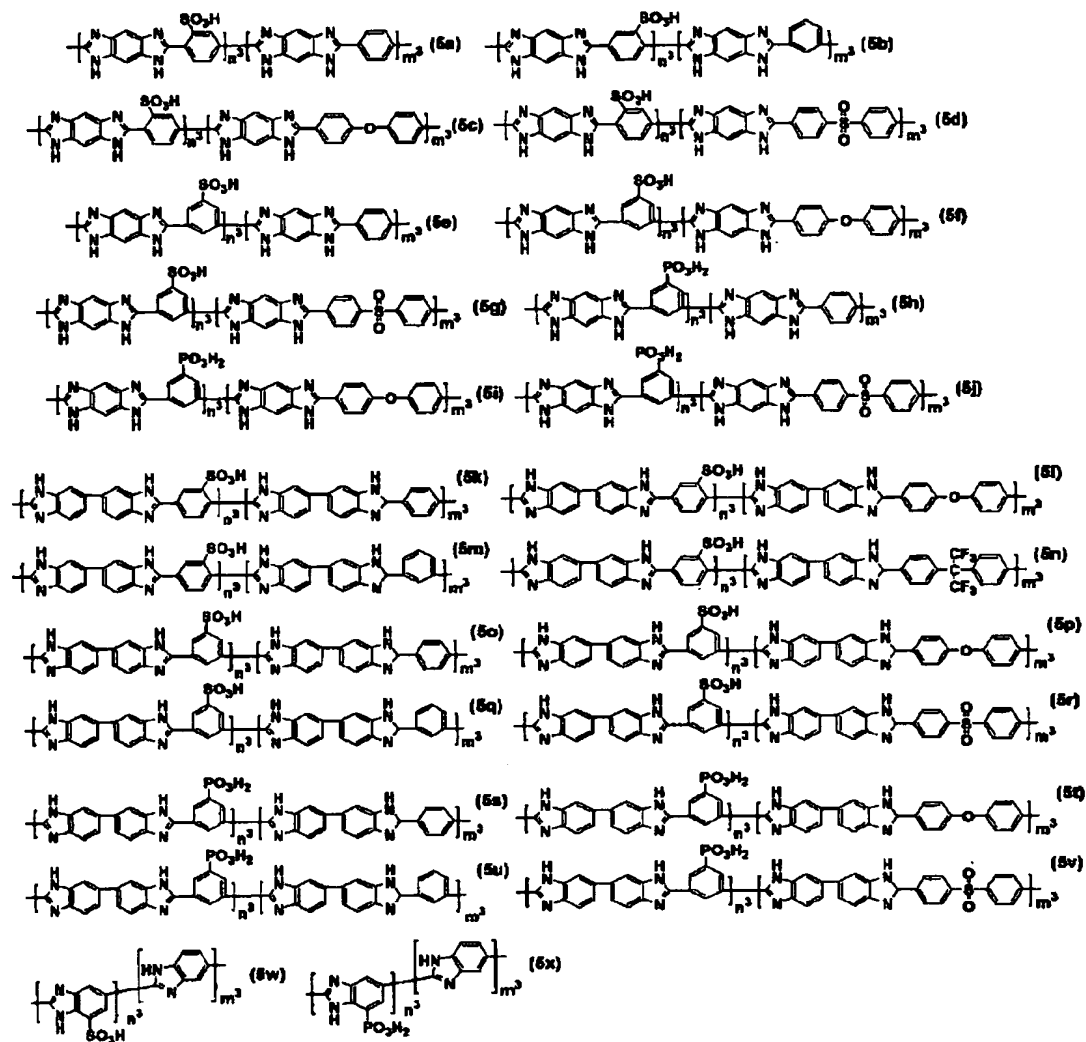
[0018] (4a), (4c), (4e), and (4g) are desirable especially. These polymers are compoundable by the approach of well-known arbitration. For example, a screw (ortho aminophenol) compound can be obtained by being among dehydration solvents, such as polyphosphoric acid, carrying out heating stirring, and making the dicarboxylic acid which has a sulfonic group and a phosphonic acid radical react. The obtained polymer can be used by the well-known approach, separating and refining it. These polymers may be any of a homopolymer, a block copolymer, and a random copolymer (when *m*₁ or *m*₂ is 0), and can be used according to the purpose.

[0019] Although a part of the sulfonic group and phosphonic acid radical in the acid polymer of this invention may form metal ions, such as sodium, a potassium, magnesium, calcium, barium, aluminum, iron, titanium, and copper, a low-molecular amine, an imidazole compound, a pyridine derivative, a quinoline derivative, etc. and the salt, it is desirable that the rate of a salt is less than [20 mol %], and it is still more desirable that it is less than [10 mol %].

[0020] The basic polymer which has an acidic group in this invention can use what has an acidic group for the basic polymer structure of well-known arbitration. As an example, the copolymer of a vinyl amine, the copolymer of a vinyl sulfonic acid and a vinyl amine, and vinyl phosphonic acid, The copolymer of a vinyl amine and an acrylic acid, the sulfonation object of Pori (4-vinylpyridine), The copolymerization object of 4-vinylpyridine and a vinyl sulfonic acid, the copolymerization object of 4-vinylpyridine and vinyl phosphonic acid, The sulfonation object of Pori (2-vinylpyridine), the sulfonated polybenzimidazole, the aromatic series system polymer (polyether sulphone --) which has the sulfonated poly quinoline, the sulfonated poly quinoxaline, a pyridine ring, a quinoline ring, and a quinoxaline ring The polybenzimidazole which can mention the sulfonation object of polysulfone, a polyether, a polysulfide, the poly ketone, a polyether ketone, and a polyether ether ketone etc., and has a sulfone radical, the poly quinoline, and the poly quinoxaline are desirable. Although desirable structure is shown below, it is not limited to these.

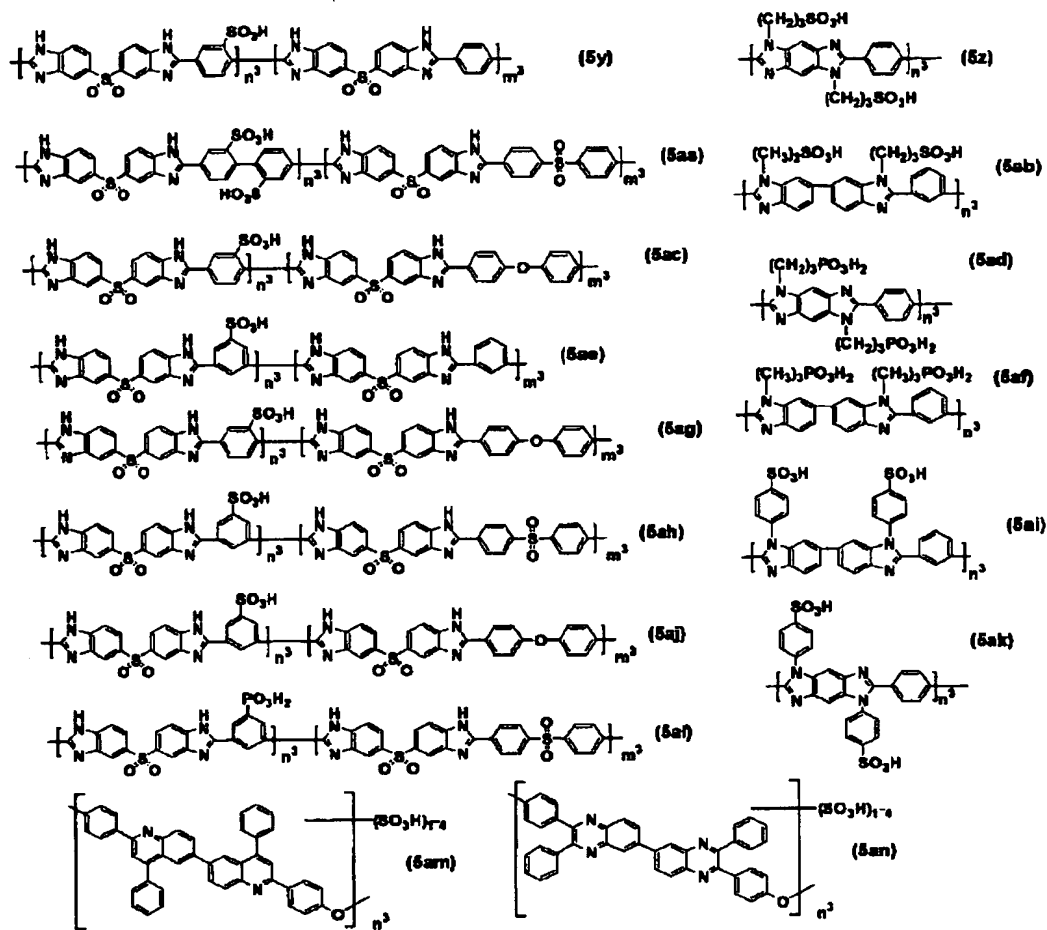
[0021]

[Formula 16]



[0022]

[Formula 17]



[0023] The basic polymer which has these acidic groups can embellish a well-known basic polymer chemically, can also compound it, and can also compound it by the polymerization using the monomer which has an acidic group. It is installation of the phosphonic acid radical which passes through sulfonation by the Krol sulfuric acid, a sulfuric anhydride oleum, etc., and chloromethylation by chloro methyl ether as a former example, and the approach of introducing a sulfonic group and a phosphonic acid radical by making an alkyl ape ton, an alkyl halide phosphonic acid derivative, an alkyl halide sulfonic-acid derivative, etc. react, after ionizing the approach of compounding from polybenzimidazole, polyvinyl pyridine, the poly quinoline, and the poly quinoxaline and polybenzimidazole by the alkali-metal hydride etc. is mentioned. As the latter approach, 2-sulfo terephthalic acid, 2, 5-dicarboxy benzene phosphonic acid, 2, a 5-disulfo terephthalic acid, 2, 5-dicarboxy 1, 4-benzene diphosphonic acid, Which sulfo or a phospho terephthalic acid, 4-sulfoisophtharate, 5-sulfoisophtharate, 4, 6-disulfo isophthalic acid, 3, 5-dicarboxy benzene phosphonic acid, 2, 4-dicarboxy benzene phosphonic acid, 4, 6-dicarboxy - 1, 3-benzene diphosphonic acid, Which sulfo or phospho isophthalic acid, a screw (4-carboxy-3-sulfophenyl) sulfone, A screw (4-carboxy-2-sulfophenyl) sulfone, the screw (4-carboxy-3-sulfophenyl) ether, The screw (4-carboxy-2-sulfophenyl) ether, 4, 4'-dicarboxy - 3 3'-disulfo bends phenon, Screw (4-carboxy-2-sulfophenyl) methane, 2, and 2-screw (4-carboxy-2-sulfophenyl) propane, Screw (4-carboxy-2-sulfophenyl) sulfide, 2, and 2-screw (4-carboxy-3-sulfophenyl) hexafluoropropane, 1, 5-disulfo - 2, 6-naphthalene dicarboxylic acid, 2-sulfo - 1, 4-naphthalene dicarboxylic acid, 4, 8-disulfo - Phospho [2, 6-naphthalene dicarboxylic acid, 4, 8-JIHOSUHO -2, 6-naphthalene dicarboxylic acid / 6-] - The approach of compounding polybenzimidazole by using acidic group content dicarboxylic acid, such as 1 and 4-naphthalene dicarboxylic acid, as a raw material etc. is mentioned.

[0024] Although the amount of the acidic group in the basic polymer which has an acidic group can take any value, it is the range of 0.1 - 5.0 meq/g preferably. It is 1.0 - 3.0 meq/g more preferably. As for the molecular weight of the poly benzoxazole which has an acidic group or the poly bends thiazole, and the basic polymer which has an acidic group, it is desirable that it is the range of 1000-10 million, and it is more desirable that it is the range of 10000-1 million. A viscosity determination is simple although measurement of molecular weight can be performed by the approaches of well-known arbitration, such as a gel partition-

chromatography method, osmometry, light scattering measurement, and a viscosity determination. as an example of a viscosity determination -- a logarithm -- measurement of viscosity is indicated in the example. the case of upright (5a) linear molecules, such as a polymer (4a), -- a logarithm -- viscosity -- the range of 0.1-100.0 -- more -- desirable -- the range of 1.0-50.0 -- it is the range of 3.0-30.0 still more preferably. the case of flexibility (5q) molecules, such as a polymer (4ab), -- a logarithm -- it is more desirable that the range of the range of viscosity being 0.1-10.0 is 0.5-5.0 preferably. If any polymer has too small molecular weight, endurance, a dynamics property, etc. will get worse, if molecular weight is too large, solution viscosity etc. will become large and workability etc. will get worse.

[0025] although the amount of the basic polymer which has an acidic group to the poly benzoxazole or the poly bends thiazole which has an acidic group can take the amount of arbitration -- the mol of the acidic group of poly benzoxazole or the poly bends thiazole -- the mol of the basic group of a basic polymer which has an acidic group to a number -- the polymer electrolyte which was excellent in endurance and ion conductivity in it being further 20 - 50 desirable% that a number is for 10 - 100% can be obtained. As for the molecular weight of the poly benzoxazole which has an acidic group or the poly bends thiazole, and the basic polymer which has an acidic group, it is desirable that it is the range of 1000-10 million, and it is more desirable that it is the range of 10000-1 million. A viscosity determination is simple although measurement of molecular weight can be performed by the approaches of well-known arbitration, such as a gel partition-chromatography method, osmometry, light scattering measurement, and a viscosity determination. as an example of a viscosity determination -- a logarithm -- measurement of viscosity is indicated in the example. the case of upright (5a) linear molecules, such as a polymer (4a), -- a logarithm -- it is desirable that the range of viscosity is 0.1-100.0, it is more desirable that it is the range of 1.0-50.0, and it is desirable that it is the range of 3.0-30.0. the case of flexibility (5q) molecules, such as a polymer (4ab), -- a logarithm -- it is more desirable that the range of the range of viscosity being 0.1-10.0 is 0.5-5.0 preferably. If any polymer has too small molecular weight, endurance, a dynamics property, etc. will get worse, if molecular weight is too large, solution viscosity etc. will become large and workability etc. will get worse.

[0026] The approach of well-known arbitration can be taken in mixing of the amount of a basic polymer which has the poly benzoxazole or the poly bends thiazole which has an acidic group, and an acidic group. You may mix in the solvent which dissolves both both, since either is made into the salt, both can be mixed, and it can also return from a salt by the acid or alkali treatment after that. Both may be mixed under existence of a low-molecular acid or a base among a solvent.

[0027] The polymer electrolyte of this invention is extruded from a mixed solution or the isolated polymer electrolyte, and it can fabricate by the approach of arbitration, such as spinning, rolling, and the cast, on fiber or a film, or it can be used for a coating ingredient etc. In case it fabricates, it is desirable to fabricate from the solution which dissolved in the suitable solvent. As a dissolving solvent, although strong acid [, such as a non-proton polar solvent, and polyphosphoric acid, methansulfonic acid a sulfuric acid trifluoroacetic acid,], such as N,N-dimethylacetamide, N.N-dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, and a hexa methyl HOSUHON amide, can be used, it is not limited to these. Plurality may be mixed and used for these solvents in the possible range. Moreover, it is good as a means which raises solubility also considering what added Lewis acid, such as a lithium bromide, a lithium chloride, and an aluminum chloride, to the organic solvent as a solvent. As for the polymer concentration in a solution, it is desirable that it is 0.1 - 30% of the weight of the range. If too low, a moldability will get worse, and if too high, workability will get worse. It is 0.5 - 5 % of the weight preferably.

[0028] The method of acquiring a Plastic solid from a solution can use a well-known approach. For example, by immersion to the polymer non-solvent with which it can mix with the solvent which dissolves heating, reduced pressure drying, and a polymer etc., a solvent can be removed and the Plastic solid of an ionicity radical content polymer can be acquired. When a solvent is an organic solvent, it is desirable to make a solvent distill off by heating or reduced pressure drying. When a solvent is strong acid, being immersed in water, a methanol, an acetone, etc. is desirable. Under the present circumstances, it can also fabricate in the form compounded with other polymers if needed on fiber or a film. When it combines with the poly azole system polymer which is excellent in thermal resistance or a mechanical property, it is convenient for carrying out good shaping.

[0029] The desirable approach of fabricating the polymer electrolyte membrane of this invention is the cast from the solution of a polymer electrolyte. A solvent can be removed from the solution which carried out the cast as mentioned above, and an electrolyte membrane can be obtained. As for removal of a solvent, being based on desiccation is desirable from membranous homogeneity. Moreover, in order to avoid decomposition and deterioration of a polymer and a solvent, it is desirable to dry at the lowest possible

temperature under reduced pressure. A glass plate, a Teflon (trademark) plate, etc. can be used for the substrate which carries out the cast. When the viscosity of a solution is high, if a substrate and a solution are heated and the cast is carried out at an elevated temperature, the viscosity of a solution can fall and the cast can be carried out easily. Although especially the thickness of the solution at the time of carrying out the cast is not restricted, it is desirable that it is 10-1000 micrometers. When too thin, it becomes impossible to maintain the gestalt as film, and the uneven film will become easy to be made if too thick. It is 100-500 micrometers more preferably. The approach of controlling the cast thickness of a solution can use a well-known approach. For example, using an applicator, a doctor blade, etc., it can be made fixed thickness, or cast area can be fixed using a glass petri dish etc., and thickness can be controlled by the amount and concentration of a solution. The solution which carried out the cast can obtain the more uniform film by adjusting the removal rate of a solvent. For example, when heating, in the first phase, it can be made low temperature and a vapor rate can be lowered. Moreover, when immersed in non-solvents, such as water, it is suitable in air and inert gas, time amount neglect of the solution is carried out, and the coagulation rate of a polymer can be adjusted.

[0030] Although the film of this invention can be made into the thickness of arbitration according to the purpose, from an ion conductivity field, a thing thin as much as possible is desirable. It is desirable that it is specifically 200 micrometers or less, and it is still more desirable that it is 10-50 micrometers.

[0031] Since the polymer electrolyte of this invention is excellent in ion conductivity and endurance, it is suitable for making it the shape of a film and film and using it as proton exchange film, such as a fuel cell. Furthermore, it can also use by using the polymer of this invention as a principal component as binder resin when producing the zygote of the polymer electrolyte membrane of this invention, and an electrode. Since the film / electrode zygote using the polymer electrolyte membrane of this invention have low internal resistance and high endurance, it can raise the generating efficiency of a fuel cell, and endurance greatly.

[0032] The solid-state polyelectrolyte film / electrode zygote of this invention carried out the hotpress of a catalyst metal and the binding material to the polyelectrolyte film, sprayed the polymer electrolyte of this invention on the commercial gas diffusion electrode, or applied, was made to permeate, and can be joined and obtained on both sides of the aforementioned polyelectrolyte film. Moreover, a catalyst bed can be carried out inside, the hotpress of what carried out the laminating of the polymer electrolyte and catalyst of this invention by the repeat of spreading desiccation of the paste which distributed to homogeneity at the solvent can be carried out to resin films, such as Teflon, polypropylene, polyethylene, and polyethylene terephthalate, on both sides of the polyelectrolyte film, and it can also join to them. Moreover, a solvent can be dried and it can also join, after applying to a polyelectrolyte the paste which distributed the polymer polyelectrolyte and catalyst of this invention to homogeneity at the solvent by the brush, the brush, the applicator, spraying, printing, etc. Moreover, electrode material, such as carbon paper, and the polymer electrolyte membrane of this invention may be joined with this paste. Since these approaches make the ionicity radical alkali-metal salts, such as Na, beforehand, they may be performed, and they may carry out returning to the acid of a basis by the acid treatment after junction. As for the concentration of a solution or the polymer electrolyte under paste, it is desirable that it is 0.1 - 10 % of the weight. Moreover, a direct catalyst is also joinable to a polymer electrolyte membrane with sputtering etc.

[0033] A catalyst may consist of a conductive ingredient which supported the particle of a catalyst metal, and may contain other components. Metals are noble metals which use platinum as a principal component, and may contain other metals, such as a rhodium, palladium, gold, silver, iridium, and a ruthenium. As for the particle size of a catalyst, it is desirable that it is the range of 1-50nm. As for the amount of the catalyst over a polyelectrolyte, it is desirable that it is 50 - 1000% of range. As other components, a polytetrafluoroethylene and tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer, a tetrafluoroethylene-hexafluoro ethylene copolymer, etc. are mentioned as binding material.

[0034] Although the conditions of a hotpress can choose suitable conditions with the ingredient to be used, it is desirable that press temperature is 100-300 degrees C, and a press pressure is the range of 1-10MPa.

[0035]

[Example] Although this invention is concretely explained using an example below, this invention is not limited to these examples. Various measurement was performed as follows.

[0036] (Ion conductivity measurement) the probe (product made from Teflon) top for its original work measurement -- the front face of a strip-of-paper-like film sample -- a platinum wire (diameter: 0.2mm) -- pressing -- the constant temperature of 80-degree-C95%RH -- an alternating current impedance [in / a sample is held in - constant humidity oven (Nagano Science Equipment Mfg. Co., Ltd., LH-20-01), and / 10kHz between platinum wires] -- SOLARTRON1250FREQUENCY RESPONSE It measured by

ANALYSER. The distance between electrodes was changed, it measured and the conductivity which canceled the contact resistance between the film and a platinum wire by the following formulas from the distance between electrodes and the inclination which plotted the resistance measurement value was computed.

- polymer electrolyte membrane conductivity [S/cm] = -- the inclination between 1 / [film width cm] x [thickness cm] x resistance poles [Ω /cm]

- Film / electrode zygote conductivity (S/cm) = the resistance (Ω) / electrode surface product of (Thickness cm) / film (cm²)

[0037] (Polymer a logarithm viscosity) About the polymer concentration of 0.05g / methansulfonic acid solution of dl, it measured at 25 degrees C using the Ostwald viscometer.

[0038] (Waterproof trial) 50mg of polymer electrolyte membranes was enclosed into glass ampul with 5ml ion exchange water. Ampul was heated for three days at 105 degrees C. The ampul after cooling was opened and the solid was separated with the glass filter of 1G2. Reduced pressure drying of the filter was carried out at 80 degrees C overnight, and from the weight before and behind filtration, it found the weight of solid content and calculated weight percentage reduction.

Weight percentage reduction [%] = residue weight [mg] / 50x100 [0039] (Quantum of an ionicity radical) It was immersed in 50ml of 0.01-N NaOH water solutions, and 100mg of polymer electrolyte membranes was stirred at 25 degrees C overnight. Then, the neutralization titration was carried out in the 0.05-N HCl water solution. a neutralization titration -- the Hiranuma Sangyo Co., Ltd. make -- potentiometric titration equipment COMTITE-980 were used. Ionicity radical weight is calculated by the following formula.

Ionicity radical content [meq/g] = (10-titration value [ml])/2 [0040] (Heat-resistant evaluation) the Shimadzu thermogravimetric analysis machine -- using TGA-50, for 10 minutes, the temperature up of about 2mg sample polymer was carried out the rate for 10-degree-C/, and it was measured after predrying at 100 degrees C under the argon ambient atmosphere. Temperature of the point of inflection of a weight change curve was made into heat loss-in-quantity initiation temperature.

[0041] (Example 1) m1/n1=0 and a logarithm -- poly benzoxazole (4a) 0.140g which has the acidic group which is viscosity 5.3 dl/g, and a logarithm -- heating stirring of the 30ml dimethyl sulfoxide (it omits Following DMSO) was carried out at 60 degrees C, and the basic polymers [0.028g and 0.06g] (5ae) triethylamine which has the acidic group which is viscosity 1.2 dl/g was dissolved. After filtering a solution with 1G2 glass filter, it flowed into the glass flat bottom petri dish with a diameter of 90mm, and subsequently reduced pressure drying was carried out for one day at 100 degrees C for two days by 40 degrees C, respectively, and DMSO was removed. The exfoliative film is 1N stirred gently. It processed for one day at the room temperature in a HCl water solution. The film was rinsed with ion exchange water and processed in 100-degree C ion exchange water for 1 hour. Then, the film was taken out and it dried under the nitrogen air current. The coefficient of water absorption when the obtained film being immersed in 25-degree C ion exchange water on the 1st was 85 % of the weight to membranous dry weight. The various evaluation results about the film are shown in Table 1.

[0042] (Examples 2-16) The polymer and the mixing ratio were changed, and also the film was produced in the same procedure as an example 1, and various evaluations were performed. An evaluation result is shown in Table 1.

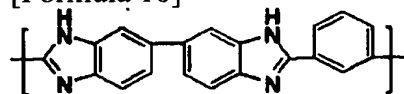
[0043] (Example 17) m1/n1=0 and a logarithm -- 10ml methansulfonic acid (it omits Following MSA) was stirred at the room temperature, and acid polymer (4a) 0.140g which is viscosity 5.3 dl/g, and polymer (5o) 0.030g were dissolved. After filtering a solution with 1G2 glass filter, it cast by the thickness of 600 micrometers on the bottom glass plate of nitrogen-gas-atmosphere mind. After leaving it under nitrogen-gas-atmosphere mind then for 1 hour, it was immersed in ion exchange water and it was made to solidify. The obtained film was immersed in ion exchange water for several days, exchanging ion exchange water until the acid was no longer detected. Then, the film was fixed to the metallic frame and it dried under the nitrogen air current. An evaluation result is shown in Table 1. The transparency IR spectrum of the film measured using the 270by Hitachi, Ltd.-30 form infrared spectrophotometer is shown in drawing 1.

[0044] (Examples 19-28) The polymer and the mixing ratio were changed and also the film was produced in the same procedure as an example 17. An evaluation result is shown in Table 1.

[0045] (Example 23) The paste was adjusted to glycerol 5g by carrying out mixed distribution so that it might become homogeneity about carbon black (particle diameter is 20-30nm) 0.72g and 1g (Du Pont; "20% of Nafion (trademark) solutions") of Nafion (trademark) solutions whose amount of platinum support is 20wt(s)%. By spraying the obtained paste with a spray, it applied to one field of the polymer electrolyte membrane obtained in the example 1, and reduced pressure drying was carried out. Reduced pressure drying

of the paste was applied and carried out also like another field. The amount of platinum support of the obtained /electrode zygote was 0.5 mg/cm². When this conductivity was measured, it was 1.5x10⁻³ S/cm. [0046] (Examples 1-2 of a comparison) Instead of the basic polymer which has an acidic group, it is the following structure.;

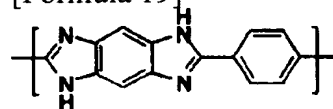
[Formula 18]



N,N-dimethylacetamide (it omits Following DMAc) was used as the solvent using ** polybenzimidazole (it omits Following PBI), and also the film was produced like the example. An evaluation result is shown in Table 1.

[0047] (Example 3 of a comparison) Instead of the basic polymer which has an acidic group, it is the following structure.;

[Formula 19]



** polybenzimidazole (it abbreviates to p-PBI below) was used, and also the film was produced like the example. An evaluation result is shown in Table 1.

[0048] (Example 4 of a comparison) Various evaluations were performed about Nafion (trademark)112 (Du Pont make) which is a commercial ion exchange membrane. An evaluation result is shown in Table 1.

[0049]

[Table 1]

No.	(a)酸性基を有する ポリベンズオキサゾール 又はポリベンズイミダゾール			(b)酸性基を有する 塩基性ポリマー			(b)の(a)に 対する 重量比	混合 溶媒	膜厚 (μm)	IEC (meq/g)	イオン 伝導性 (S/cm)	耐熱性 (℃)	耐水性 (%)	
	構造	m/n	対数粘度 (dl/g)	構造	m/n	対数粘度 (dl/g)								
実施例1	4a	0.00	6.4	5aa	0.00	1.7	0.200	DMSO	20	2.87	0.54	390	92	
実施例2					0.00	1.7	0.300		22	2.93	0.51	390	90	
実施例3		0.10	7.5		0.00	1.7	0.300		21	3.01	0.58	390	89	
実施例4					0.10	1.9	0.200		21	2.54	0.29	390	95	
実施例5	4a	0.10	3.3		0.00	1.7	0.300		20	2.67	0.34	390	92	
実施例6					0.10	1.9	0.200		19	2.87	0.44	390	93	
実施例7	4i	0.00	1.7		0.00	1.7	0.200		21	2.78	0.71	390	94	
実施例8					0.00	1.7	0.300		22	2.66	0.67	390	88	
実施例9		0.10	3.2		0.10	1.9	0.200		21	2.99	0.44	395	90	
実施例10					0.10	1.9	0.300		23	2.50	0.34	390	87	
実施例11	4a	0.00	6.4	5ai	0.00	1.8	0.300	DMSO	20	2.99	0.29	390	88	
実施例12					0.10	2.2	0.200		20	2.88	0.34	390	90	
実施例13	4a	0.10	3.3		0.00	1.8	0.300		22	2.85	0.40	390	94	
実施例14					0.10	2.2	0.200		20	2.78	0.48	390	92	
実施例15	4i	0.10	3.2		0.00	1.8	0.300		MSA	22	2.82	0.38	390	99
実施例16					0.10	2.2	0.200			19	2.81	0.39	390	94
実施例17	4a	0.00	6.4	0.00	2.3	0.300	21	2.88		0.78	390	95		
実施例18				0.10	1.9	0.200	21	3.01		0.34	390	90		
実施例19	4a	0.10	3.3	5k	0.00	2.3	0.300	24		3.15	0.70	390	87	
実施例20					0.10	1.9	0.200	21		2.85	0.48	390	94	
実施例21	4i	0.10	3.2		0.00	2.3	0.300	23	2.79	0.45	390	97		
実施例22					0.10	1.9	0.200	20	2.98	0.61	390	88		
実施例23	4a	0.00	6.4		0.00	1.9	0.300	MSA	21	2.78	0.45	395	99	
実施例24					0.10	1.7	0.200		21	2.80	0.61	395	97	
実施例25	4a	0.10	3.6	0.00	1.9	0.300	24		3.05	0.65	395	85		
実施例26				0.10	1.7	0.200	21		2.75	0.40	395	97		
実施例27	4i	0.10	3.2	0.00	1.9	0.300	MSA		23	2.89	0.35	395	98	
実施例28				0.10	1.7	0.200			20	2.86	0.49	395	92	
比較例1	4a	0.00	6.4	PBI	-	1.5	0.300	DMSO /DMAc	20	2.12	0.05	390	90	
比較例2	4a	0.10	3.3		-		-		0.300	21	2.05	0.02	390	91
比較例3	4i	0.10	3.2		p-PBI		-		10.1	0.200	MSA	19	2.03	0.04
比較例4	Nafion112			-	-	-	-	-	60	1.10	0.15	300	98	

[0050]

[Effect of the Invention] With the polymer electrolyte of this invention, the polymer electrolyte excellent in ion conductivity and endurance, a polymer electrolyte membrane, the film / electrode zygote can be offered.

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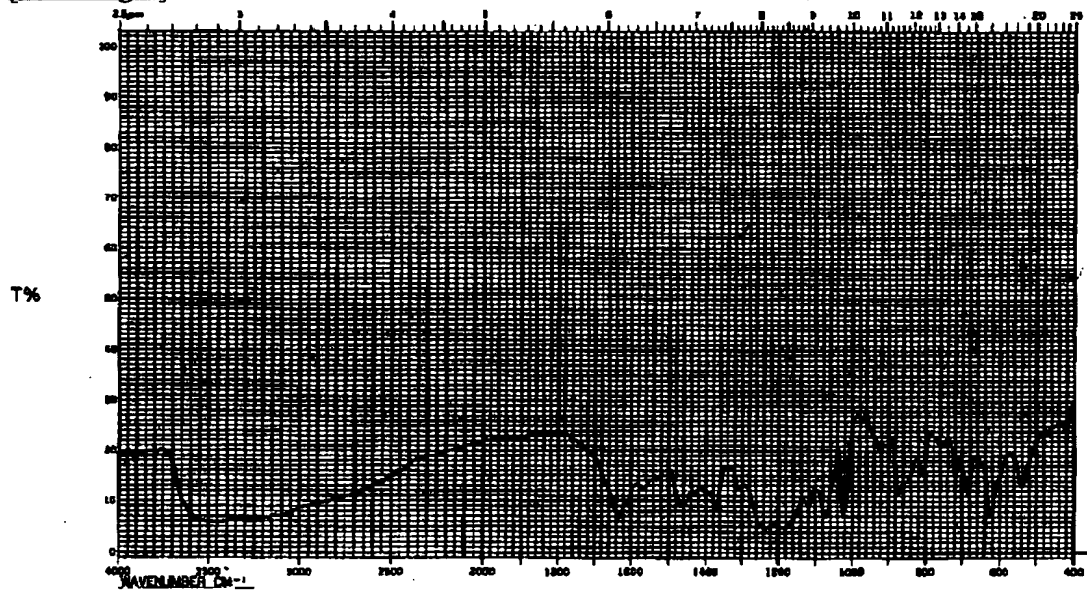
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2. **** shows the word which can not be translated.
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DRAWINGS

[Drawing 1]



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PATENT ABSTRACTS OF JAPAN

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(54) BLENDED POLYMER ELECTROLYTE, ELECTROLYTIC MEMBRANE HAVING THE ELECTROLYTE AS MAIN COMPONENT, AND MEMBRANE /ELECTRODE JUNCTION CONTAINING THE ELECTROLYTE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyelectrolyte superior in ionic conductivity and durability and suitable for a proton exchange membrane or the like of a fuel cell, and provide an electrolytic membrane having the electrolyte as the main component, and a membrane/electrode junction containing the electrolyte.

SOLUTION: This is a blended polymer electrolyte composed of a mixture of (a) polybenzoxazole or polybenzthiazole having not less than one kind of groups selected from a sulfonic acid group and its salts or a phosphonic acid group and its salts, and (b) a basic polymer having at least one kind of groups selected from groups composed of a sulfonic acid group and its salts, a phosphonic acid group and its salts, and a carboxylic acid group and its salts.

リキノキサリンからなる群より選ばれた1種以上の化合物であることを特徴とする、請求項1又は2に記載のプロレンドポリマー電解質。

【請求項4】 請求項1～3のいずれかに記載のプレンドポリマー電解質を主成分とする電解質膜。

【請求項5】 請求項1～3のいずれかに記載のプレンドポリマー電解質膜を、膜及びノズル又は電極層に含むことを特徴とする膜/電極接合体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、高分子電解質膜として有用なポリマー電解質、それを主成分とする電解質膜、及び該電解質を用いた膜/電極接合体に関するものである。

【0002】

【従来の技術】 液体電解質のかわりに高分子固体電解質をイオン伝導体として用いる電気化学的装置の例として、水電解槽や燃料電池を挙げることができる。これらに用いられる高分子膜は、カチオン交換膜としてプロトン導電率と共に化学的、熱的、電気化学的及び力学的に十分安定なものでなくてはならない。このため、長期にわたって使用できるものとしては、主にメチルフェニル型「ナフィオン（登録商標）」を代表例とするパーフオロカーボンスルホン酸膜が使用されてきた。しかしながら、100℃を超える条件で運転しようとする、この含水率が急激に落ちる他、膜の軟化も顕著となる。このため、将来が期待されるメタノールを燃料とする燃料電池においては、膜内のメタノール透過による性能低下が起こり、十分な性能を発揮することはできない。また、現在主に検討されている水系を燃料として80℃付近で運転する燃料電池においても、膜のコストが高すぎることが燃料電池技術の確立の障害として指摘されている。

【0003】 パーフオロカーボンスルホン酸膜に代わる電解質膜として、ポリエーテルエーテルケトンやポリエーテルスルホン、ポリスルホンなどのポリマーにスルホン酸基など酸性基を導入した、いわゆる炭化水素系ポリマー電解質が近年盛んに検討されている。しかしながら、炭化水素系ポリマー電解質はパーフオロカーボンスルホン酸に比べて水吸・膨潤しやすく、高湿度下での耐久性に問題があった。

【0004】 膨潤を抑制する方策の一つとして、塩基性ポリマーとの混合が行なわれている。これは、ポリマー電解質中のスルホン酸基などの酸性基を、塩基性ポリマーによって架橋すること膨潤を抑制しようとするものである。例えば、スルホン酸基を有するポリエーテルスルホンとスルホン酸基を有するポリエーテルケトン（酸性ポリマー）と、ポリベンズイミダゾール（塩基性ポリマー）との混合物（国際公開特許公報W099/54389号公報）などが知られている。しかしながら、スルホン化ポリエーテルスルホンやスルホン化ポリ

エーテルエーテルケトンには、酸や熱によるスルホン酸基の脱離が起こりやすく耐久性が充分ではなかった。

【0005】 一方、国際公開特許公報W001/01510号公報では、2,5-ジフルオロ-3,6-ジスルホテトラフルエンや、2,2'-ジスルホ-4,4'-ジフェニルエーテルカルボン酸を用いたポリベンズイミダゾールとポリベンズイミダゾールの混合物からなる膜が記載されているが、そのイオン伝導性に関しては記載されていない。

【0006】 米国特許公報第5998550号にはスルホン酸基を有するポリベンズイミダゾールと塩基性の熱硬化性化合物との分子複合体が、米国特許公報第5439号にはスルホン酸基を有するポリベンズイミダゾールと塩基性の熱可塑性ポリマーとの分子複合体が、それぞれ記載されているが、いずれにおいても電解質なド電気化学的用途に関しては述べられていなかった。また、スルホン酸基を有するポリベンズイミダゾールは、パーフオロカーボンスルホン酸や、スルホン酸基を有するポリスルホン、ポリエーテルスルホン、ポリエーテルエーテルケトンなどの他のポリマー電解質よりもイオン伝導性が低いという欠点があった。

【0007】 一般に、酸性ポリマーに塩基性ポリマーを混合することで耐久性は向上するものの、同時に酸性ポリマーが本来有していたイオン伝導性を犠牲にするものがあった。

【0008】

【発明が解決しようとする課題】 本発明の目的は、燃料電池のプロトン交換膜などに好適な、イオン伝導性と耐久性に優れた高分子電解質、該電解質を主成分とする電解質膜、及び該電解質を含む膜/電極接合体を提供することにある。

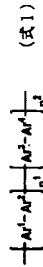
【0009】

【課題を解決するための手段】 本発明者らは、上記目的を達成するために鋭意研究を重ねた結果、酸性基を有するポリベンズオキサゾール又はポリベンズチアゾールと酸性基を有する塩基性ポリマーを混合することによって、耐久性、イオン伝導性などに優れた性能を示すポリマー電解質、電解質膜、及び膜/電極接合体が得られることを見出し、本発明の完成に至った。

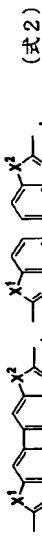
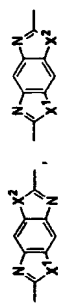
【0010】 すなわち本発明は、

(1) (a) スルホン酸基及びその塩、又はホスホン酸基及びその塩の塩からなる群より選ばれた一種以上の基を分子中に1個以上有するポリベンズオキサゾール又はポリベンズチアゾールと、(b) スルホン酸基及びその塩、ホスホン酸基及びその塩、カルボン酸基及びその塩、ホスホン酸基及びその塩からなる群より選ばれた一種以上の基を分子中に1個以上有する塩基性ポリマーとの混合物からなるプレンドポリマー電解質、(2) ポリベンズオキサゾール又はポリベンズチアゾールが下記一般式(1)又は(5)；

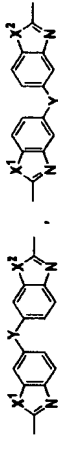
【化6】



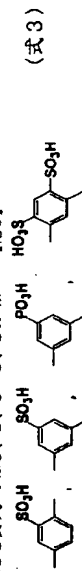
【式(1)】は、Ar¹及びAr²からなる繰り返し単位と、Ar³及びAr⁴からなる繰り返し単位とが、ランダムと、Ar³及びAr⁴からなる繰り返し単位とが、ランダムと、



(式2)

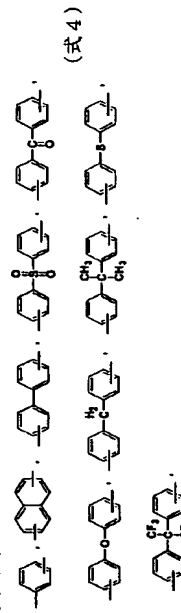


で表される残基より選ばれた一種以上の残基を表し、A ※2、C (CH₃)₂、C (CF₃)₂、S (=O)₂のいずれr¹とAr²は同一であっても異なってもよい。X¹かを表す。Ar²は下記一般式(3)；及びX²はO又はSを表す。YはO、S、C=O、CH ※【化8】



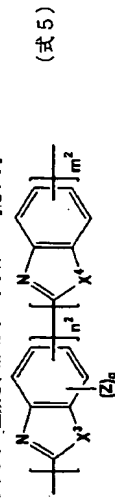
(式3)

で表される群より選ばれた一種以上の残基を表す。Ar² ★【化9】
4は下記一般式(4)； ★



(式4)

で表される残基よりなる群より選ばれた一種以上の残基 ※000の数をそれぞれ表す。]
を表す。n¹は1～10000の整数を、m¹は0～10 ★【化10】

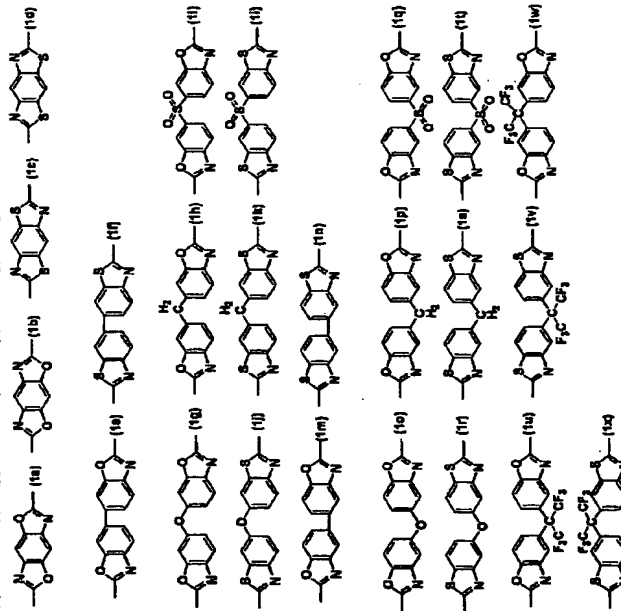


(式5)

【式(5)】は、それぞれの繰り返し単位が、ランダム又はブロックで連結していることを表す。式中、X³及びX⁴は5原子又は6原子のいずれかを表し、これらは同一であっても異なってもよい。Zは、SO₃H基、PO₃H₂基、及びそれらの塩から選ばれた一種以上の基を表す。qは1～3の整数を、n²は1～10000の整数を、m²は0～10000の整数をそれぞれ表す。】で表されることを特徴とする(1)に記載のプレンドポリマー電解質であり、並びに、(3) 塩基性ポリマーが、2-ビニルピリジンとその共重合体、ポリベンズイミダゾール、ポリキノリン、ポリキノキサリンからなる群より選ばれた一種以上の化合物であることを特徴とする、(1)又は(2)に記載のプレンドポリマー電解質であり、並びに、(4) (1)～(3)のいずれかに記載のプレンドポリマー電解質を主成分とする電解質膜であり、並びに、(5) (1)～(3)のいずれかに記載のプレンドポリマー電解質膜を、膜及びノズル又は電極層に含むことを特徴とする膜/電極接合体、である。

リマーが、2-ビニルピリジンの重合体及びその共重合 50 【0011】

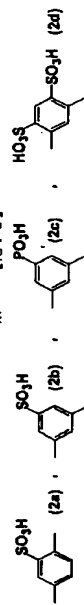
【発明の実施の形態】以下本発明について詳細に説明する。一般式(1)における Ar^1 及び Ar^2 の好ましい例*



が挙げられるがこれに限定されるものではない。より好ましいのは(1b)、(1c)、(1e)、(1f)、(1g)、(1i)であり、最も好ましいのは(1b)、(1c)である。

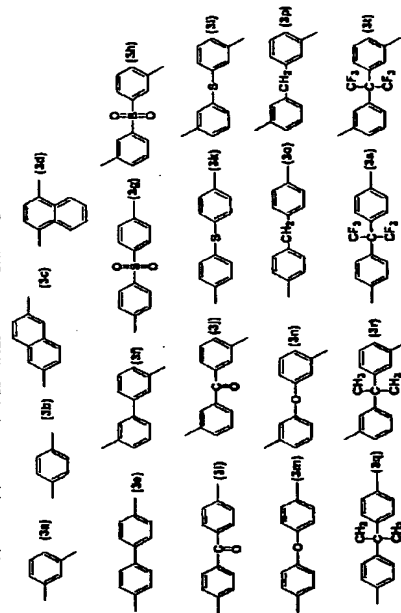
【0012】 Ar^2 の酸性基としては、スルホン酸基、ホスホン酸基、カルボン酸基、及びそれらの塩を挙げることができる。中でもスルホン酸基、ホスホン酸基が好ましく、スルホン酸基がイオン伝導性を高めるためにより好ましい。塩を構成する化合物としては、ナトリウム、カリウム、マグネシウム、カルシウム、バリウム、アルミニウム、鉄、チタン、銅などの金属イオンや、低分子のアミン、イミダゾール化合物、ピリジン誘導体、キノリン誘導体などが挙げられる。全酸性基中の塩は、0~99モル%の間にあることが好ましく、20モル%以下であることがより好ましく、10モル%以下であることがさらに好ましい。酸性基の個数は1個以上であり、2個以上であってもよい。スルホン酸基とホスホン酸基などのように異なる酸性基が併存していてもよい。

※ 【化12】



※ 【0013】芳香族基とは、1個以上の芳香族環を含む基を表す。芳香族基中には、炭素数1~6のアルキル基と、ベンゼン環、ナフタレン環などの炭化水素基の他に、ピリジン環、キノリン環などの芳香族複素環も含まれる。 Ar^2 中に、ハロゲン元素が共有結合で結合していると廃棄時に環境に悪影響を及ぼすため、 Ar^2 は共有結合で結合しているハロゲン元素を含まないことが好ましい。酸性基は、芳香族環に直接又はアルキル基などの他の有機基を介して結合していることが好ましい。酸性基の脱離を抑制するため、酸性基が結合している芳香族環には、アルキル基、エーテル基、アミノ基などの電子供与性基が結合していないことが好ましい。特に限定されるものではないが、 Ar^2 の好ましい例として、下記の構造(2a)~(2d)で表される基を挙げることができる。

中でも(2a)がより好ましい。
【0014】 Ar^4 の好ましい例としては、下記の残基* 【化13】

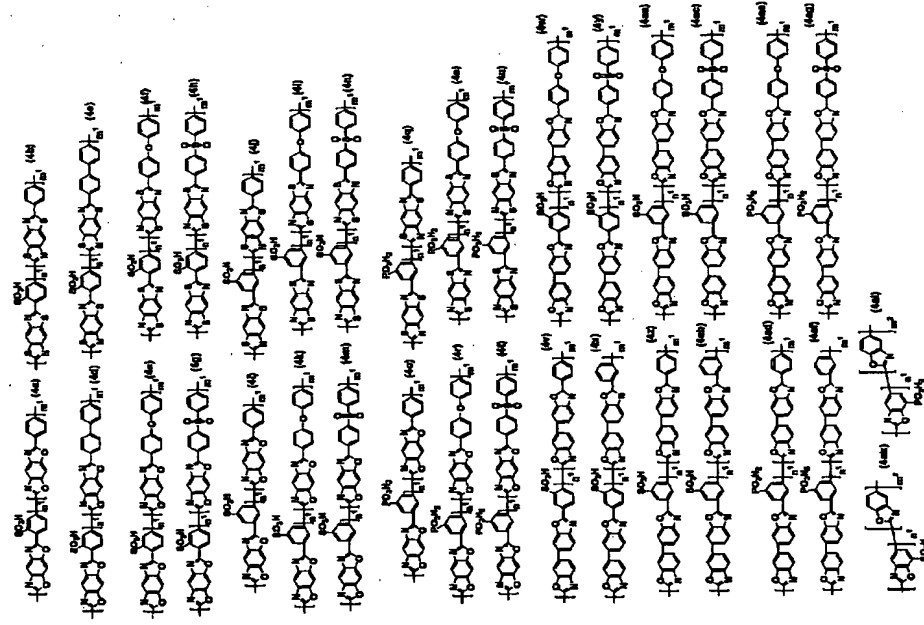


を挙げることができ、これらに限定されるものではない。20であることがさらに好ましい。また、m1及びm2は任意の値であってよいが、m1/n1又はm2/n2が0~0.5の間であると、イオン伝導性が高くなるためより好ましく、0~0.2の間であることがさらに好ましい。

【0015】 X^3 及び X^4 はOであることがより好ましく、いずれもOであることがイオン伝導性を高めるために最も好ましい。Zはスルホン酸基又はその塩であることが好ましい。n¹及びn²は10以上であると成型体が好ましい力学特性を示すためより好ましく、100以上

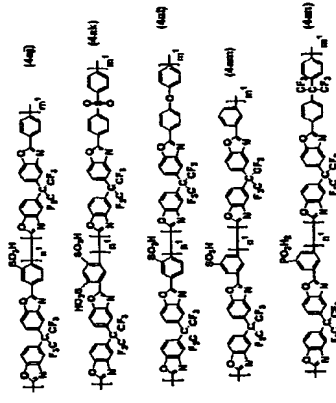
【0016】本発明における酸性ポリマーの好ましい例を以下(4a)~(4n)に示すが、これらに限定されるものではない。

【化14】



【0017】

【化15】



【0018】中でも好ましいのは(4a)、(4c)、(4e)、(4g)である。これらのポリマーは公知の任意の方法で合成することができる。例えば、ビス(オアミノフェノール)化合物を、スルホン酸基やホスホン酸基を有するジカルボン酸とを、ポリリン酸などの脱水縮合中で加熱攪拌して反応させることで得ることができる。得られたポリマーは公知の方法で分離、精製して使用することができる。これらのポリマーは、ホモポリマー(m'又はm''が0の場合)、ブロックコポリマー、ランダムコポリマーのいずれであってもよく、目的に応じて使用することができる。

【0019】本発明の酸性ポリマーにおける、スルホン酸基及びホスホン酸基の一部が、ナトリウム、カリウム、マグネシウム、カルシウム、バリウム、アルミニウム、鉄、チタン、銅などの金属イオンや、低分子のアンモニウムイオン、ピリジン誘導体、キノリン誘導体などと塩を形成していても良いが、塩の割合が20モル%以下であることが好ましく、10モル%以下であることがさらに好ましい。

【0020】本発明における酸性基を有する塩基性ポリ

マーは、公知の任意の塩基性ポリマー構造に酸性基を有するものを使用することができる。例としては、ビニルアミンとビニルスルホン酸の共重合体、ビニルアミンとビニルホスホン酸の共重合体、ビニルアミンとアクリル酸の共重合体、ポリ(4-ビニルピリジン)のスルホン化物、4-ビニルピリジンとビニルスルホン酸の共重合体、ポリ(2-ビニルピリジン)のスルホン化物、スルホン化したポリベンズイミダゾール、スルホン化したポリキノリン、スルホン化したポリキノリン誘導体、スルホン化したポリベンズイミダゾール、スルホン化したポリキノリン誘導体及びキノリン誘導体を有する芳香族系ポリマー(ポリエーテルスルホン、ポリスルホン、ポリエーテル、ポリスルホニド、ポリケトン、ポリエーテルケトン、ポリエーテルエーテルケトン)のスルホン化物などを挙げることができる。スルホン基を有するポリベンズイミダゾール、ポリキノリン、ポリキノリン誘導体、ポリキノリン誘導体、好ましい構造を以下に示すがこれらに限定されるものではない。

【0021】

【化16】

TGA-50を用いて、約2mgのサンブルポリマーを、アルゴン雰囲気下で100℃で10分間予熱乾燥の後、10℃/分の速度で昇温して測定した。重量変化曲線の変曲点の温度を熱減量開始温度とした。

【0041】(実施例1) $m/n=0$ 、対酸粘度5.3dl/gである酸性基を有するポリベンゾキサゾール(4a) 0.140g、対酸粘度1.2dl/gである酸性基を有する塩基性ポリマー(5ae) 0.028g、0.06gのトリエチルアミンを30mlのジメチルスルホキシド(以下DMSOと略する)を60℃で加熱撹拌して溶解した。溶液を1G2ガラスフィルターで濾過した後、直径9.0mmのガラス製平板シャーレに注ぎ、40℃で2日間、次いで100℃で1日間それぞれ減圧乾燥してDMSOを除去した。剥離した膜は、ゆるやかに撹拌した1N HCl水溶液中室温で1日間処理した。膜はイオン交換水で水洗し、100℃のイオン交換水中で1時間処理した。その後、膜を取りだし、窒素気流下で乾燥した。得られた膜を、25℃のイオン交換水に1日浸漬したときの吸水量は、膜の乾燥重量に対して85重量%であった。膜についての各種評価結果を表1に示す。

【0042】(実施例2~16) ポリマーと混合比を変更した他は、実施例1と同様の手順で膜を製作し、各種評価を行なった。評価結果を表1に示す。

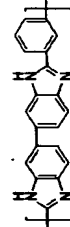
【0043】(実施例17) $m/n=0$ 、対酸粘度5.3dl/gである酸性ポリマー(4a) 0.140g、ポリマー(5o) 0.030gを10mlのメタンスルホン酸(以下MSAと略する)を室温で撹拌して溶解した。溶液を1G2ガラスフィルターで濾過した後、窒素雰囲気下ガラス板上に600μmの厚みで流延した。そのまま窒素雰囲気下で1時間放置した後、イオン交換水に浸漬して凝固させた。得られた膜は、酸が抽出されなくなるまでイオン交換水を交換しつつ、数日間イオン交換水に浸漬した。その後、膜を金属性の枠に固定し、窒素気流下で乾燥した。評価結果を表1に示す。(株)日立製作所製270-30形赤外分光光度計を用いて測定した膜の透過IRスペクトルを図1に示す。

【0044】(実施例19~28) ポリマーと混合比を変更した他は、実施例17と同様の手順で膜を製作し

た。評価結果を表1に示す。

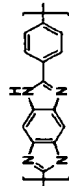
【0045】(実施例23) 白金担持量が20wt%であるカーボンブラック(粒子径が20~30nm) 0.72gとナフイオン(登録商標)溶液(デュボン社製；「ナフイオン(登録商標)溶液20%」) 1gを均一になるようにグリセリン5gに混合分散することによってペーストを調整した。得られたペーストをスプレーにより噴霧することによって実施例1で得たポリマー電解質膜の一方の面に塗布し、減圧乾燥した。もう一方の面にも同様にペーストを塗布し、減圧乾燥した。得られた/電極接合体の白金担持量は0.5mg/cm²であった。この導電率を測定したところ1.5×10⁻⁸S/cmであった。

【0046】(比較例1~2) 酸性基を有する塩基性ポリマーの代わりに、下記の構造；



【化18】
のポリベンズイミダゾール(以下PBIと略する)を用い、その溶媒としてN、N-ジメチルアセトアミド(以下DMAcと略する)を用いた他は、実施例と同様に膜を製作した。評価結果を表1に示す。

【0047】(比較例3) 酸性基を有する塩基性ポリマーの代わりに、下記の構造；



【化19】
のポリベンズイミダゾール(以下p-PBIと略する)を用いた他は、実施例と同様に膜を製作した。評価結果を表1に示す。

【0048】(比較例4) 市販のイオン交換膜であるNafion(登録商標)112(デュボン社製)について各種評価を行なった。評価結果を表1に示す。

【0049】
【表1】

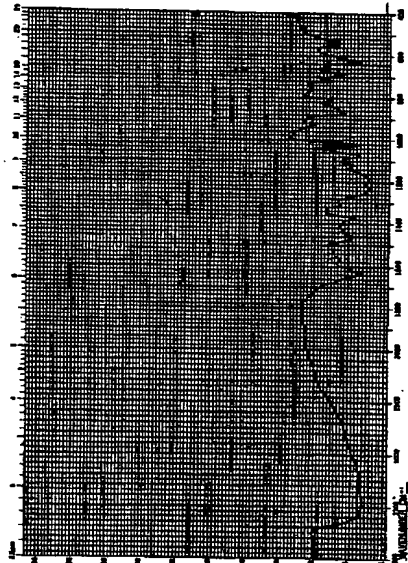
No.	(a)酸性基を有するポリベンゾキサゾール(4)の平均分子量	(b)酸性基を有する塩基性ポリマー(5)の平均分子量	(c)酸性基を有する塩基性ポリマー(5)の平均分子量	混合溶媒	膜厚 [μm]	IEC (mmol/g)	イオン伝導性 (S/cm)	耐水性 (%)		
実施例1	4	0.00	0.00	0.00	0.00	20	2.81	0.54	350	82
実施例2	4	0.00	0.00	0.00	0.00	22	2.83	0.51	350	85
実施例3	4	0.10	0.10	0.10	0.00	21	2.81	0.58	350	88
実施例4	4	0.10	0.10	0.10	0.00	21	2.84	0.59	350	85
実施例5	4	0.10	0.10	0.10	0.00	20	2.81	0.54	350	82
実施例6	4	0.10	0.10	0.10	0.00	18	2.81	0.44	350	82
実施例7	4	0.10	0.10	0.10	0.00	22	2.84	0.57	350	88
実施例8	4	0.00	0.00	0.00	0.00	22	2.84	0.57	350	88
実施例9	4	0.10	0.10	0.10	0.00	23	2.80	0.44	350	80
実施例10	4	0.10	0.10	0.10	0.00	23	2.80	0.44	350	80
実施例11	4	0.00	0.00	0.00	0.00	20	2.83	0.54	350	88
実施例12	4	0.00	0.00	0.00	0.00	20	2.88	0.54	350	88
実施例13	4	0.10	0.10	0.10	0.00	22	2.85	0.40	350	84
実施例14	4	0.10	0.10	0.10	0.00	20	2.78	0.48	350	82
実施例15	4	0.10	0.10	0.10	0.00	22	2.85	0.48	350	88
実施例16	4	0.10	0.10	0.10	0.00	18	2.81	0.35	350	84
実施例17	4	0.00	0.00	0.00	0.00	21	2.88	0.78	350	85
実施例18	4	0.00	0.00	0.00	0.00	21	2.88	0.78	350	85
実施例19	4	0.10	0.10	0.10	0.00	24	3.14	0.70	350	87
実施例20	4	0.10	0.10	0.10	0.00	21	2.85	0.48	350	84
実施例21	4	0.10	0.10	0.10	0.00	23	2.79	0.48	350	84
実施例22	4	0.10	0.10	0.10	0.00	20	2.84	0.51	350	88
実施例23	4	0.00	0.00	0.00	0.00	21	2.78	0.45	350	88
実施例24	4	0.10	0.10	0.10	0.00	21	2.80	0.41	350	87
実施例25	4	0.00	0.00	0.00	0.00	24	3.05	0.85	350	85
実施例26	4	0.10	0.10	0.10	0.00	21	2.75	0.40	350	87
実施例27	4	0.00	0.00	0.00	0.00	23	2.89	0.88	350	88
実施例28	4	0.10	0.10	0.10	0.00	20	2.84	0.48	350	82
比較例1	4	0.00	0.00	0.00	0.00	20	2.84	0.85	350	87
比較例2	4	0.10	0.10	0.10	0.00	21	2.85	0.40	350	84
比較例3	4	0.10	0.10	0.10	0.00	20	2.84	0.45	350	88
比較例4	4	0.00	0.00	0.00	0.00	20	2.80	0.45	350	88

【0050】

【発明の効果】 本発明のポリマー電解質により、イオン伝導性と耐久性に優れたポリマー電解質、ポリマー電解

質膜、膜/電極接合体を提供することができる。
【図面の簡単な説明】
【図1】 実施例17で得られた膜のIRスペクトル。

【図1】



【手続補正書】
【提出日】平成14年6月19日（2002.6.19）
【手続補正1】
【補正対象書類名】明細書
【補正対象項目名】0044
【補正方法】変更
【補正内容】
【0044】（実施例1と28）ポリマーと混合比を変更した他は、実施例17と同様の手順で膜を作製した。評価結果を表1に示す。
【手続補正2】
【補正対象書類名】明細書
【補正対象項目名】0045
【補正方法】変更
【補正内容】
【0045】（実施例25）白金担持量が20wt%であるカーボンブラック（粒子径が20～30nm）0.72gとナフィオン（登録商標）溶液（デュポン社製；「ナフィオン（登録商標）溶液20%」）1gを均一になるようにグリセリン5gに混合分散することによってペーストを調整した。得られたペーストをスプレーにより噴霧することによって実施例1で得たポリマー電解質膜の一方の面に塗布し、減圧乾燥した。もう一方の面にも同様にペーストを塗布し、減圧乾燥した。得られた電極接合体の白金担持量は0.5mg/cm²であった。この導電率を測定したところ、5×10⁻³S/cmであった。

フロントページの続き
(51)Int.Cl.⁷ F I 7-70-1 (参考)
H 01 M 8/10 H 01 M 8/10